

mechanical strength, and also other properties such as abrasion resistance depending on usages.

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## Disclosure of the Invention

### Problems to be solved by the Invention

[0007] The present invention has been achieved in view of the above-described problems and provides a phenolic resin molding material excelling in moldability, heat resistance, dimensional accuracy and mechanical strength.

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[0008] The present invention also provides a phenolic resin molding material excelling in abrasion resistance as well as moldability, heat resistance, dimensional accuracy and mechanical strength.

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### Means for solving the Problems

[0009] The present inventors have made a devoted study in order to remedy the above-described problems and achieved the present invention by finding that a target molding material can be obtained by blending phenolic novolak, which has a small amount of a monomeric phenol and a dimeric phenol and has a narrow molecular weight distribution, with an inorganic filler at a specified ratio.

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[0010] Specifically, the phenolic resin molding material of the present invention comprises blending 450 to 900 parts by mass of an inorganic fibrous filler with 100 parts by mass of phenolic novolak in that a total content of a monomeric phenol and a dimeric

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phenol is 10% or less measured by the area method of gel filtration chromatography and a degree of dispersion ( $M_w/M_n$ ) of a weight-average molecular weight ( $M_w$ ) and a number-average molecular weight ( $M_n$ ) is 1.1 to 3.0 when measured by gel filtration chromatography, wherein the inorganic fibrous filler is a combination of wollastonite and glass fiber, the blending amount of the wollastonite is 350 to 800 parts by mass, and the blending amount of the glass fiber is 100 to 200 parts by mass.

## 10 Effects of the Invention

[0011] The phenolic resin molding material of the present invention has outstanding moldability, heat resistance, dimensional accuracy and mechanical strength. Therefore, molded parts formed of this molding material are favorably used as alternatives to automobile parts and various types of metallic parts which are required to have heat resistance and dimensional accuracy.

[0012] Especially, the phenolic resin molding material having a fibrous filler blended as an inorganic filler of the present invention has good moldability regardless of the reduction in resin amount and also has outstanding heat resistance,  
5 dimensional accuracy, mechanical

ethylene glycol monobutyl ether, ethylene glycol monopentyl ether, ethylene glycol dimethyl ether, ethylene glycol ethylmethyl ether and ethylene glycol monophenyl ether.

[0025] Examples of the cyclic ether are 1,3-dioxane,  
5 1,4-dioxane and the like, examples of the polyalcohol-based ether are glycol esters such as ethylene glycol acetate, examples of the ketones are acetone, methyl ethyl ketone, methyl isobutyl ketone and the like, and examples of the sulfoxide are dimethyl sulfoxide, diethyl sulfoxide and the like.

10 [0026] Among them, methanol, ethylene glycol monomethyl ether, polyethylene glycol and 1,4-dioxane are particularly desirable.

[0027] The reactive cosolvents are not limited to the above-described examples but solid types can also be used if they  
15 have the above-described properties and are in a state of liquid at the time of the reaction. And, they can be used alone or as a combination of two or more. The reactive cosolvent is not limited to a particular blending amount but used in 5 parts by mass or more, and preferably 10 to 200 parts by mass, per 100 parts  
20 by mass of phenol.

[0028] An amount of water in the reaction system has an effect on a phase separation effect and a production efficiency but is generally 40% or less according to the mass standard. If the amount of water exceeds 40%, there is a possibility that the  
25 production efficiency decreases.

[0029] A reaction temperature between the phenol and the aldehyde is significant to enhance the phase separation effect and generally 40°C to a reflux temperature, preferably 80°C to a

reflux temperature and more preferably a reflux temperature. If the reaction temperature is less than 40°C, the reaction time becomes very long, and the low-molecular weight component cannot be reduced. The reaction time is variable depending on the  
5 reaction temperature, blending amount of phosphoric acid, a moisture content in the reaction system and the like but generally about 1 to 10 hours. As a reaction environment, normal pressure is suitable, but the reaction may be made under pressure or under a reduced pressure if the heterogeneous reaction which is a  
10 feature of the present invention is maintained.

[0032] The inorganic fibrous filler used in the present invention is not limited to a particular one. For example, among calcium carbonate, clay, talc, silica, fibrous ones and also fibrous fillers of wollastonite, potassium titanate and aluminum borate, various types of carbon fibers such as pitch-based and PAN-based fibers, aramid fiber, glass fiber and the like can be used. But, it is desirable that the wollastonite is selected to improve the abrasion resistance and heat resistance and the glass fiber is selected to improve the mechanical strength and heat resistance and not to degrade the abrasion resistance, and they are combined. This combination is also desirable in view of the cost performance.

[0033] The blending amount of the inorganic fibrous filler is 450 to 900 parts by mass, preferably 600 to 800 parts by mass, to 100 parts by mass of the phenolic novolak. And, the wollastonite is used in 350 to 800 parts by mass, preferably 450 to 700 parts by mass, and the glass fiber is used in 100 to 200 parts by mass, preferably 110 to 150 parts by mass. If the inorganic fibrous filler is less than 450 parts by mass, the resin amount increases, so that the abrasion resistance degrades, and a coefficient of linear expansion becomes high. Therefore, the thermal shock property (heat resistance) by a sharp change in temperature tends to degrade. And, if the inorganic fibrous filler is more than 900 parts by mass, there are problems that the fluidity becomes poor, and it is difficult to secure the stable moldability. Thus, the blending amount falling outside of the above-described range is not desirable.

[0034] To the phenolic resin molding material of the present

invention can be added various types of additives, which are conventionally used for the phenolic resin molding material, for example a curing agent such as hexamethylenetetramine, a mold release agent such as calcium stearate or zinc stearate, a curing  
5 accelerator such as magnesium oxide, a coupling agent, a solvent and the like as desired.

[0035] A method of producing the phenolic resin molding material of the present invention is not limited a particular one,

isobutyl ketone was completely removed by vacuum distillation to obtain 213.5 parts of phenolic novolak (1).

[0040] [Production of phenolic novolak (2)]

In a reactor provided with a thermometer, a stir device and  
5 a condenser were charged 193g of phenol, 142g of 37% by mass formalin (F/P=0.85) and 0.97g of oxalic acid (0.5%/P), a temperature was gradually raised to a reflux temperature (98 to 102°C), a condensation reaction was conducted at the same temperature for six hours, and vacuum concentration was made to  
10 obtain 199g of phenolic novolak (2) (yield of 103%/P).

[0041] [Properties of phenolic novolak]

The properties of the obtained phenolic novolak were measured by the following test methods. The results are shown in Table 1.

15 [0042] (I) Degree of dispersion

Using Tosoh Corporation's gel filtration chromatography SC-8020 series build-up system (column: G2000H<sub>x1</sub>+G4000H<sub>x1</sub>, detector: UV 254 nm, carrier: tetrahydrofuran 1 ml/min, column temperature: 38°C), a weight-average molecular weight (Mw) and  
20 a number-average molecular weight (Mn) were determined in terms of standard polystyrene equivalent, and a degree of dispersion (Mw/Mn) was calculated.

[0043] (II) a monomeric phenol and a dimeric phenol contents (%)

The areas of the monomeric phenol and the dimeric phenol  
25 to the total area of molecular weight distribution were measured by the area method which indicates in percentage.



[0044] [Table 1]

	Phenolic novolak (1)	Phenolic novolak (2)
Number-average molecular weight(Mn)	755	512
Weight-average molecular weight(Mw)	1227	3842
Degree of dispersion (Mw/Mn)	1.63	7.5
Monomeric phenol content(%)	0.3	9.1
Dimeric phenol content(%)	3.3	8.4

[0045] &lt;Example 1&gt;

As shown in Table 2, 100 parts of phenolic novolak (1), 400 parts of wollastonite (a product of TOMOE Engineering Co., Ltd.,

5 NYAD 400, reference fiber diameter:  $7\mu\text{m}$ ,

aspect ratio: 4) and 167 parts of glass fiber (a product of Nitto Boseki Co., Ltd., reference fiber diameter:  $11\mu\text{m}$ , average fiber length: 3 mm) as inorganic fibrous fillers, 16 parts of hexamethylenetetramine and 15 parts of a mold release agent and 5 others were blended and mixed uniformly. Then, the mixture was kneaded uniformly into a sheet form under heating by heated rolls, cooled, and crushed by a power mill to obtain a granular molding material.

[0046] The obtained molding material was injection-molded under the following conditions to obtain a JIS shrink test specimen, a JIS bending test specimen (80×10×4 mm), and an abrasion testing ring test specimen.

5 [0047]Cylinder temperature: front 85°C, rear 40°C

Mold temperature: 175°C

Curing time: 60 seconds

[0048] The obtained test specimen was subjected to after-curing at 210°C for 20 hours, and evaluated for the  
10 following properties. The results are shown in Table 2.

[0049] (1) Bending strength

Measured according to JIS K 7203.

(2) Thermal shock

The piston model having the dimensions and shape shown in  
15 Fig. 1 was heated at 300°C for 30 minutes, immediately removed and put under water of 23°C, and test specimens were examined for their appearances. This procedure was repeated for five cycles. After the five cycles, the test specimens free from a crack were determined to be good.

20 (3) Resistance to hot water

JIS shrink test specimens were immersed in hot water of 80°C for 500 hours, and dimensional change rates after the immersion were measured.

(4) Abrasion resistance

25 The test was conducted under the following conditions, and the abrasion testing ring test specimens and counterpart materials were measured for abrasion wear.

Test load: 60 kg/cm<sup>2</sup>

Test rate: 0.1 m/s

Test time: 2 hours

Counterpart material: FCD450

Test environment: Under brake oil (normal temperature)

5 [0051] <Example 2, Comparative Examples 1 to 3>

Molding materials were produced in the same way as in Example 1 except that the blending ratios were changed as shown in Table 2, and evaluation was conducted. The results are shown in Table 2. Comparative Example 2 had poor roll workability, and a molding  
10 material could not be obtained.

[0061] [Table 2]

		Example 1	Example 2	Comparative Example 1	Comparative Example 2	Comparative Example 3
Blending composition[parts]	Phenolic novolak (1)	100	100	—	—	100
	Phenolic novolak (2)	—	—	100	100	—
	Hexamethylenetetramine	16	15	16	16	16
	Wollastonite	400	750	200	400	200
	Glass fiber	167	100	100	167	100
	Calcium stearate	5	5	5	5	5
	Carbon black	7	7	7	7	7
	Magnesium oxide	3	—	3	—	3
Roll workability		○	○	○	×	○
Bending strength(Mpa)		150	120	130	—	135
Thermal shock		Good	Good	Cracked by 1 cycle	—	Cracked by 1 cycle
Resistance to hot water(%)		+0.03	+0.02	+0.18	—	+0.17
Abrasion resistance	Test specimen(mg)	3	2	12	—	18
	Counterpart material(mg)	1	0	4	—	6
Performance						

[0062] It is apparent from Table 2 that the phenolic resin molding materials obtained in Examples have well-balanced properties of heat resistance (thermal shock resistance), abrasion resistance, dimensional accuracy and mechanical strength.